QUARTERLY REVIEWS

RADIATION CHEMISTRY OF HYDROCARBONS

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CHEMICAL reactions wrought by ionising radiation involve a broad spectrum of labile intermediates; whilst this consideration underlies the complexity of the subject, it also serves to promote intrinsic interest. Ionisation in radiation chemistry refers to the removal of a valency-shell electron from a molecule. The parent molecule-ion can be regarded as a positively charged free radical, and it represents an important intermediate species: from this standpoint, it is convenient to group ionisation with the more familiar heterolysis and homolysis.

$$\begin{array}{lll} RX \rightarrow RX^{+\cdot} & + e^- & \text{Ionisation} \\ RX \rightarrow R^+ & + X^- & \text{Heterolysis} \\ RX \rightarrow R\cdot & + X\cdot & \text{Homolysis} \end{array}$$

Except for compounds of metallic ions, odd-electron positive ions derived from molecules are rare in conventional chemistry, and only a few species are usually described,[1] such as the Würster salts derived from *p*-phenylenediamine, where delocalisation of the odd electron confers unusual stability on the ion-radical. In general, the energy requirement for ionisation (Table 1) is too high to be easily achieved by thermal or chemical means, for solvation can make little contribution to this process. However, some possible exceptions to this rule for oxygen and nitrogen compounds are discussed elsewhere.[2]

The positive molecule-ion is derived most readily from hydrocarbons by electron or charged-particle impact, and in many cases it is an intermediate of great reactivity. In addition to ions, various electronically excited states of neutral molecules are also formed directly by electron impact, and possibly by neutralisation, but at the present time there is little quantitative information as to the potential reactivity of excited states for large polyatomic molecules. In this Review, an outline is given of the quantitative theory of molecule-ion reactions, with particular emphasis on the rates and energetics of the unimolecular and bimolecular processes which lead to the formation of molecules, uncharged free-radicals, and secondary

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[1] Waters, "The Chemistry of Free Radicals," Clarendon Press, Oxford, 1946, p. 75.

[2] Ff. Williams, *J. Amer. Chem. Soc.*, 1962, **84**, 2895.

ions.[3,4] The advantage of this approach is that it provides a valuable frame of reference for much, although not all, of the subsequent discussion, which is concerned with the experimental results from radiation chemistry and their interpretation, Hydrocarbons form an appropriate subject for an integrated discussion of radiochemical reactions. Because of their technological importance, there exists an extensive literature on the fundamental chemistry of these compounds; and in particular the properties of related ions and free radicals have been thoroughly explored.

1. Historical Introduction

The historical development of radiation chemistry is worthy of more than casual attention, for it reflects the shifting interests and interpretations which have marked the growth of this subject. After the discovery of *X*-rays and radioactive elements at the end of the nineteenth century, much interest was aroused by the chemical effects of the various radiations. In a series of papers,[5] Sir William Ramsay described the decomposition of several simple gases in the presence of radon, and remarked that, "whenever radium emanation produces chemical action, then, other conditions being unaltered, each particle of emanation as it disintegrates produces the same amount of change". This conclusion embodies the relation between energy absorption and chemical change which provides the primary datum in radiation chemistry. In the modern usage introduced by Burton,[6] the *G*-value is defined as the yield of molecular change per 100 electron-volts of absorbed energy.

Among the earlier studies, the work of Lind[7] and of Mund[8] deserves special recognition, for it marks the beginning of careful quantitative studies on gaseous reactions: even in the wake of very recent research, much of this pioneering effort remains a reliable source of accurate information. Since the irradiation techniques involved the use of radon, it was natural for these investigators to relate the observed chemical change to the amount of ionisation produced in the system. Thus the term M/N is used to express the number of molecules that reacted, or were formed, per ion-pair, and this quantity therefore illustrates the connection between the physical and the chemical actions of radiation. The *G*-value and M/N are related by the expression,

$$G = \frac{100}{W} \cdot \frac{M}{N}$$

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[3] Stevenson and Schissler, "The Chemical and Biological Action of Radiations," Academic Press, London, 1961, Vol. V, pp. 170—270.

[4] Field and Franklin, "Electron Impact Phenomena," Academic Press, New York, 1957; Lampe, Franklin, and Field, "Progress in Reaction Kinetics," Vol. I, Pergamon Press, London, 1961, p. 69.

[5] Cameron and Ramsay, *J.*, 1908, 966, and later papers.

[6] Burton, *Discuss. Faraday Soc.*, 1952, **12**, 317.

[7] Lind, "Radiation Chemistry of Gases," Reinhold Publ. Co., New York, 1961.

[8] Mund, "Actions Chimiques et Biologiques des Radiations," Masson et Cie, Paris, 1956, Vol. II, p. 39.

where W is defined as the mean energy required to form one ion-pair in irradiated gases. Reactions showing large departures from M/N values of unity or thereabouts were deemed to have special characteristics. In particular, high M/N values, as obtained with acetylene and other unsaturated compounds, were ascribed to the formation of molecular clusters around the primary positive ion. As we shall describe later, there is much evidence, both new and old, to support the existence of "ion-molecule clusters," but such a mechanism of gaseous polymerisation is probably far from unique. Notable experimental contributions were also made by Essex[9] to the study of gaseous reactions. He recognised the possibility that part of the chemical action of high-energy radiation could arise from the reactions of electronically excited species as well as ions. In an attempt to separate these contributions, an electric field was applied up to saturation ion current; on the premise that the ions which were collected did not contribute to the residual chemistry, the latter could be attributed to the action of uncharged intermediates. Strangely enough, this technique has not been widely applied by others. One of the uncertainties of the method concerns the extent and nature of chemical change produced by the neutralisation of ions at metal electrodes.

On the theoretical side, the papers of Eyring, Hirschfelder, and H. S. Taylor[10] in 1936 still represent the most lucid and penetrating analysis of the problems which are involved. These authors discussed a number of fairly simple gaseous reactions which had been widely studied, including the hydrogen–bromine combination and ortho–para-hydrogen conversion. In the first place, they drew attention to the important fact that molecule-ions have the valency properties of free radicals. Moreover, reactions of the type,

$$H_2^{+\cdot} + H_2 \rightarrow H_3^+ + H\cdot$$

were discussed, and the rate constant was calculated by the Eyring transition-state theory. It turns out (see below) that when, some 20 years later, this ion-molecule reaction was studied in the mass spectrometer, the predicted rate constant was closely verified. Secondly, the authors emphasised the importance of neutral free radicals and atoms as chain carriers in thermal and photochemical reactions, and they argued that it was unnecessary to invoke the existence of ion–molecule clusters to explain large values of M/N. The latter comments led inadvertently to an almost complete rejection of ionic processes in radiation chemistry until the recent renaissance, arising largely from the new information on ion–molecule reactions, helped to restore the balance. The lesson of these events has been discussed by several authors, and the general conclusion is clear, namely, that reaction mechanisms based on neutral free radicals alone can often provide a superficial explanation of the gross results without revealing the more subtle and hidden factors which operate.

[9] Essex, *J. Phys. Chem.*, 1954, **58**, 42.

[10] Eyring, Hirschfelder, and Taylor, *J. Chem. Phys.*, 1936, **4**, 479, and later papers.

Radiation research received its greatest impetus as a result of the nuclear-energy projects undertaken during the Second World War. Although Fricke *et al.*,[11] Kailan,[12] and others had previously studied the irradiation of liquids, the technological needs of reactor construction and solvent-extraction processes demanded new knowledge on a variety of unexplored systems. As a by-product of this development, an increased abundance of high-intensity radiation sources, both radioactive nuclides and high-energy accelerators, became available. A large fraction of the fundamental research carried out over the past two decades has been centred on water and aqueous solutions,[13] but there is an increasing trend towards the study of organic compounds. About ten years ago, many optimistic opinions were expressed about the possibility of utilising radiation energy in promoting chemical syntheses. Except for some specialised uses in the plastics industry, few applications have materialised, and it is now generally recognised that further research must precede a more critical assessment of large-scale industrial possibilities.

2. Energy Absorption from Ionising Radiation

The photo-ionisation threshold, I, for most hydrocarbons lies between 8 ev and 13 ev; the actual value for a particular compound depending on the binding energy of the electrons in the highest molecular orbital. From this limit to the million-volt quanta obtainable from radioactive nuclides or high-energy accelerators, the physical principles governing the absorption of electromagnetic radiation are well established.[14] Here, it suffices to mention that the attenuation is caused by the photoelectric effect, Compton recoil scattering, and pair production. By these processes, electrons are ejected from the atoms or molecules of the absorber with, on the average, an appreciable fraction of the incident photon energy. The photoelectric absorption coefficient depends upon Z^4 (Z = atomic number) and diminishes with increasing photon energy, whereas pair production is a function of Z^2 and only contributes above 1 Mev. In the range of much practical interest from 200 Kev to 2 Mev, Compton scattering predominates almost exclusively for materials of low atomic number, so that the energy absorption is then simply proportional to the number of electrons per gram. γ-Rays or high-energy X-rays, therefore, constitute a source of energetic electrons which are released homogeneously throughout the exposed material. It follows that, when other factors are equal, no physicochemical differences should arise between the effects of electron-beam and photon irradiation at high energies, and there is no reliable evidence to suggest the contrary. Apart from complications attending nuclear reactions

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[11] Fricke, Hart, and Smith, *J. Chem. Phys.*, 1938, **6**, 229.

[12] Kailan, *Z. phys. Chem.*, 1920, **95**, 215.

[13] Allen, "The Radiation Chemistry of Water and Aqueous Solutions," Van Nostrand Co. Inc., Princeton, 1961.

[14] Spiers, *Discuss. Faraday Soc.*, 1952, **12**, 13.

which lie outside the scope of this Review, fast neutron beams lose energy mainly by causing nuclear recoil. Thus high-energy protons are readily generated by fast-neutron irradiation of hydrocarbons.

The detailed dissipation of all high-energy radiations is therefore due to the interaction of fast charged particles with the absorbing medium. Quantum theory regards all energy losses as occurring only in collisions whereby electrons are removed or excited from the bound levels in atoms or molecules, and the experimental results on the distribution of energy loss in different kinds of collisions[15] are in good accord with the tenets of this theory. The best theoretical description of this problem is generally accredited to Bethe,[16] but no accurate prediction is given as to the vital statistics concerning the relative importance of ionisation and excitation events. Perhaps the most useful guide comes from a comparison of W with I. The results[17,18] quoted in Table 1 reflect the generalisation that W/I always exceeds unity by an appreciable amount, and it is reasonable to infer that this excess is associated with excitation, both of the ion and of the neutral molecule.

TABLE 1

Molecule	I (ev)	Ref.	W (ev)	Ref.
CH_4	12·99	18	29·2	17
C_2H_6	11·65	18	26·6	17
C_2H_4	10·52	18	28·0	17
C_2H_2	11·41	18	27·5	17
C_6H_6	9·25	18		
n-C_6H_{14}	10·48	4		

The spatial distribution of ionisation and excitation events depends upon the charge z and velocity v of the particle moving through a medium of atomic number Z composed of N atoms per c.c. A most useful parameter is the rate of energy loss with distance, $-dT/dx$, often termed the linear energy transfer (LET), which is given by the Bethe formula,[16]

$$\frac{-\mathrm{d}T}{\mathrm{d}x} = \left(\frac{2\pi e^4 z^2 N Z}{m v^2}\right) B$$

where e and m are the charge and rest mass, respectively, of the electron, and B represents a dimensionless quantity which is a function both of the particle velocity v and the mean excitation potential $\bar{L}$ of the absorber. For the motion of heavy particles, *e.g.*, protons or α-rays,

$$B = 2 \ln (2mv^2/\bar{L}),$$

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[15] E. J. Williams, *Proc. Roy. Soc.*, 1931, *A*, **130**, 328.
[16] Bethe, *Ann. Physik*, 1930, **5**, 325; *Handb. Physik*, 1933, **24**, 273.
[17] Jesse and Sadauskis, *Phys. Rev.*, 1953, **90**, 1120.
[18] Watanabe, *J. Chem. Phys.*, 1957, **26**, 542.

but for fast electrons approaching relativistic speeds, a more complicated relation becomes applicable. These theoretical expressions are in good agreement with the experimental results, and such information allows a calculation of the presumed primary-ion distribution in liquids.[19] On this basis, a 1 Mev α-particle travelling through an aqueous system gives rise to successive primary events at a separation of only about 2 Å, whereas for a 100 Kev electron in the same medium, the spacing exceeds 2000 Å. It must be added that some of the primary events associated with the passage of fast electrons lead to the ejection of slow secondary electrons with enough energy to cause additional ionisation in close proximity, so that a group of ions is formed; the average population of these clusters is about three ions per event, and much larger clusters are infrequent. Further, electrons are occasionally ejected from atoms or molecules in the primary event with sufficient energy to produce a well-defined branch (δ-ray) off the main path. Thus the complete energy-loss spectrum for any particle includes a sizeable contribution from the subsequent degradation in energy of the secondary electrons.

The question now arises, how do the different LET properties of various charged particles affect the subsequent chemistry? For gases, the limited evidence bearing on this point suggests that LET effects are unimportant, so that the *G*-values for systems studied under identical conditions appear to be independent of the particle used and of its incident energy. For liquids, changes in LET certainly affect the radiation chemistry of water,[13] and this phenomenon has been the subject of much theoretical interpretation[20] in terms of the diffusion of the primary radicals away from their initial site of formation. Briefly, the hydrogen atoms and the hydroxyl radicals (or their equivalents, since these species may be amphoteric) have a greater probability of intercombination at high LET when they are produced in dense tracks or clusters, with the net result that the number of radicals diffusing out into the body of the solvent for homogeneous reactions with any available solute is lessened by comparison with radiation of lower LET.

There are several reasons why a similar description cannot be applied to hydrocarbon liquids. In the first place, the primary dissociation of water molecules to form hydrogen atoms and hydroxyl radicals, as originally suggested by Weiss (cf. ref. 13), can hardly be questioned, regardless of their precise mode of origin, whereas for hydrocarbons the nature of the initial processes cannot be specified unambiguously (see below). Even more important is the fact that the radicals formed from water do not enter into any net reaction with the solvent, the reason being, of course, that the high value for the bond-dissociation energy, D_{298} (H–OH) = 118·8 kcal./mole, precludes abstraction by the hydrogen atom, while the hydroxyl

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[19] Lea, "Actions of Radiations on Living Cells," Cambridge Univ. Press, 1955, 2nd edn., p. 25.

[20] Samuel and Magee, *J. Chem. Phys.*, 1953, **21**, 1080.

radical reacts with no resultant chemical change. Owing to its comparative inertness, water represents an excellent medium for the study of free-radical reactions. On the other hand, in saturated hydrocarbons, any hydrogen atoms produced by radiolysis would be expected to form hydrogen molecules quite readily by abstraction from the solvent. In fact, the radiation chemistry of liquid cyclohexane has proved to be insensitive to variation in LET.[21] The only evidence for the existence of a LET effect in hydrocarbons comes from a study of aromatic substances,[22] where it has been found that the *G*-yields for hydrogen gas, and to a smaller extent for the less volatile products, increase at high LET. It may be significant that hydrogen atoms are known to be very reactive towards aromatic compounds without forming molecular hydrogen. A more detailed discussion of the chemistry of these systems is deferred until later in this Review.

While the foregoing discussion illustrates some of the useful, but limited, information which can be derived from radiation physics, a fundamental approach to radiation chemistry requires additional understanding of the various processes following the excitation and ionisation of molecules. This is particularly the case for large polyatomic molecules where the number of possibilities for dissociation and reaction can be inconveniently large.

3. Elementary Reactions

A large fraction of the experimental work on gaseous ions has been carried out with the aid of the mass spectrometer. There has been some reluctance on the part of many to accept the validity of conclusions derived from mass spectrometry when applied to macroscopic behaviour at higher pressures. This is understandable if the argument is based solely on empirical extrapolations. However, the use of the mass spectrometer in recent years has provided a wealth of basic information[3,4] which can no longer be ignored.

(a) The Formation and Dissociation of Polyatomic Ions.—The generation of ions for mass-spectroscopic studies is usually accomplished by low-energy electron impact or photoionisation of gases at a pressure of about 10^{-5} mm. mercury. Recently,[23] a polonium α-ray source has been developed to permit studies at higher pressures (*ca.* 10^{-2} mm.); in this case, the mass-spectral patterns show interesting differences from those obtained by 70 ev electron impact. By the first two ionisation methods, the energy of the incident electrons or photons can be controlled with some precision by means of experimental refinements, and this allows the detection of ionic phenomena as a function of ionising electron energy. These methods

[21] Schuler and Allen, *J. Amer. Chem. Soc.*, 1955, **77**, 507.

[22] Burns, Wild, and Ff. Williams, Proc. 2nd U.N. Internat. Conf. Peaceful Uses of Atomic Energy (Geneva), 1958, **29**, 266.

[23] Melton and Rudolph, *J. Chem. Phys.*, 1959, **30**, 847; *J. Phys. Chem.*, 1959, **63**, 916.

permit the evaluation of the threshold ionisation potential, I, for a molecule, and also the appearance potentials corresponding to the minimum energies at which the dissociation of the parent or another fragment ion leads to the observation of daughter ions. The various extrapolation procedures which are employed in these determinations have been thoroughly reviewed.[3] In practice, the electron-impact method gives ionisation-potential values which are often a few tenths of an electron volt greater than those associated with photoionisation. The latter method,[18] and the determination by optical spectroscopy in the vacuum-ultraviolet range,[24] allow calculation of the energy difference between the vibrational ground states of the molecule and the ion (this refers to the adiabatic ionisation potential at 0°K). By comparison, electron-impact values give the vertical Franck–Condon transition energy to the lowest electronic state of the molecule-ion, so that the latter may be formed with excess of vibrational energy. For compounds such as neopentane, tetramethyl-lead, and carbon tetrachloride, where the parent-ion intensity is almost undetectable in the 70 ev mass spectrum, and only fragment ions are initially observed at low threshold ionising voltages, it seems reasonable to conclude that the missing parent ion undergoes rapid dissociation by virtue of having an excess of vibrational energy at birth.

Parent ions derived from hydrocarbon molecules undergo fragmentation by a number of different processes. It is convenient to recognise two general modes of dissociation according to whether the fragment ion retains an even or an odd number of electrons. For alkane ions, a carbonium ion and a neutral free radical may be formed or, alternatively, the products may be an olefin ion and a neutral molecule; only rarely will two atoms or two neutral free radicals be formed instead of the molecule in the latter case. For n-pentane, the following processes may be regarded as representative of the two classes:

$$\text{n-}C_5H_{12}^{+\cdot} \rightarrow C_3H_7^{+} + C_2H_5^{\cdot}$$
$$\text{n-}C_5H_{12}^{+\cdot} \rightarrow C_3H_6^{+\cdot} + C_2H_6$$

If the dissociation products are formed "adiabatically" in their electronic ground states with no excess of internal or translational energy, then the difference between the appearance potential $A(F^+)$ of the fragment ion (F^+) and the ionisation potential of the parent $I(P)$ might be expected to correspond to the minimum dissociation energy ϵ_0 for the process. Now ϵ_0 can be evaluated independently from appropriate ionisation potentials (photoionisation method) and standard thermo-chemical data. Thus, for the dissociation of the n-pentane ion to give the propyl ion and the ethyl radical, the thermochemical change is given by:

$$\epsilon_0 = I(C_3H_7\cdot) - I(\text{n}-C_5H_{12}) + D_0(C_3H_7\text{–}C_2H_5)$$

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[24] Price, *Chem. Rev.*, 1947, **41**, 257.

While apparent agreement is often reached between the values of ϵ_0 by these two procedures, implying the reliability of the electron-impact method for the direct determination of thermochemical quantities[25] in such instances, it is fair to point out that there are also exceptions to be found,[26] where the assumptions mentioned above probably do not hold. Further, any agreement between ϵ_0 values would suggest that the fragment ion is detected in the mass spectrometer at the minimum energy requirement; in general, this will not be true, for reasons to be discussed below.

The mass spectrum of a hydrocarbon[27] at 50—100 ev ionising electron energy is usually a composite of a large number of fragment peaks together with the parent. It is found that at incident electron energies greater than about $2I$, the mass spectrum is relatively insensitive to change in ionising energy. This may be taken to indicate that relatively few high-energy transfers occur when the incident energy far exceeds the molecular binding energies of the valency electrons. In analytical mass spectrometry,[28] it is the characteristic fragmentation pattern for a particular compound which serves as an empirical guide to the identification of molecular structure and the quantitative analysis of mixtures. The most constructive attempt to develop a theoretical basis for the origin of mass spectra is represented by the quasi-equilibrium unimolecular rate theory due to Eyring and his associates.[29] Because this theory has important ramifications extending to systems of direct interest in macroscopic radiation chemistry, it will be discussed briefly. In essence, this approach represents an application of the general theory of unimolecular reaction rates[30] to the problems of mass spectra. From many standpoints, the ability to make direct observations on ion dissociation processes at very low pressures offers ideal conditions for the study of unimolecular reactions. Foremost of the assumptions on which the Eyring theory rests is that any excess of electronic energy initially imparted to the polyatomic ion is converted into vibrational and rotational energy within the period of a few molecular vibrations (*ca.* 10^{-13} sec.). The basis of this postulate is the existence of a large number of electronic states for the molecule-ion; these states have low symmetry characteristics, so that a large number of crossing points become available for the equilibration of electronic energy over all the internal degrees of freedom. Thereafter, in the absence of intermolecular energy transfer, the rate of dissociation of the molecule-ion is determined by the probability of a critical amount of energy becoming localised in the bond(s) undergoing rupture or rearrangement. Thus, according to this view, the labile excited

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[25] Stevenson, *Discuss. Faraday Soc.*, 1951, **10**, 35.

[26] Wallenstein and Krauss, *J. Chem. Phys.*, 1961, **34**, 929.

[27] Catalog of Mass Spectral Data, American Petroleum Institute, Project 44.

[28] Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Van Nostrand Co. Inc., Princeton, 1960.

[29] Rosenstock, Wallenstein, Wahrhaftig, and Eyring, *Proc. Nat. Acad. Sci. U.S.A.*, 1952, **38**, 667.

[30] Kassel, "Kinetics of Homogeneous Gas Reactions," Reinhold Publ. Co., New York, 1932, Chapter 5.

ion does not undergo immediate dissociation at the moment of formation, but persists for a definite lifetime; confirmation that this is indeed the case is supplied by the existence of non-integral m/e ions, often referred to as metastable, which are formed in the analyser tube of the spectrometer after a residence time of about 10^{-5} sec. in the ionisation chamber.

Two basic criticisms can be directed at the Eyring theory. First, the assumption as to rapid energy randomisation may not apply strictly to molecules with less than about six atoms, for then the electronic levels will tend to be more discrete. Of course, the theory is entirely unnecessary and inapplicable to diatomic molecules. Secondly, energy exchange between vibrational modes of different symmetry properties may be forbidden.[31] No quantitative modifications of the theory have been suggested to deal with these limitations. For many quantitative discussions on the applicability of the theory, the simple classical form of the unimolecular rate constant has been used, *viz.*,

$$k_i(\epsilon) = \nu_i\left(1 - \frac{\epsilon_0}{\epsilon}\right)^S,$$

where $k_i(\epsilon)$ is the rate constant of process i and measures the probability for the dissociation per unit time of ions with energy ϵ (referred to the vibrational ground state), ν_i is a frequency factor related to the entropy of activation, ϵ_0 is the activation energy identified with the thermochemical-energy change for the dissociation, and S is the number of effective oscillators $= 3n\text{-}7$ for a non-linear molecule of n atoms. While the above formula has the merit of relative simplicity, it is not rigorously applicable in all cases. In order to obtain the above expression from the rigorous theory, various approximations have to be made,[32] which become especially severe at low values of ϵ/ϵ_0 and S. Further, it has been calculated[33] that the use of a more exact formulation for the unimolecular rate constant, as given by Marcus and Rice,[34] leads to significant increases in the rate constants near the threshold for low activation energies. In this light, some of the objections raised against the Eyring theory may be invalid. We shall return later to the significance of high rate constants for low values of ϵ_0.

Stevenson[35] has given a general treatment of the kinetics of parent-ion dissociation based upon the validity of the above expression for $k_i(\epsilon)$. In order for $k(\epsilon)$ to be greater than, say, 10^q, ϵ must clearly satisfy the expression,

$$10^r\left(\frac{\epsilon - \epsilon_0}{\epsilon}\right)^S \geqslant 10^q,$$

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[31] Slater, "Theory of Unimolecular Reactions," Cornell Univ. Press, Ithaca, 1959.
[32] Rosenstock, *J. Chem. Phys.*, 1961, **34**, 2182.
[33] Wolfsberg, *J. Chem. Phys.*, 1962, **36**, 1072.
[34] Marcus and Rice, *J. Phys. Colloid Chem.*, 1951, **55**, 894.
[35] Stevenson, *Radiation Res.*, 1959, **10**, 610.

where we have represented the frequency factor ν by 10^r. By re-arrangement,

$$\epsilon \geqslant \epsilon_0/(1 - 10^{(q-r)/S});$$

and let ϵ_1 be the ϵ value where the equality sign holds. This expression tells us that an ion must receive an excitation energy ϵ_1 greater than ϵ_0 if it is to undergo dissociation within a time given by 10^{-q} sec. This is the reason why dissociation processes which are only observed in the mass spectrometer after 10^{-5} sec. give $\epsilon_1(q = 5)$ rather than ϵ_0 from appearance potential differences. But this formula is also most revealing for problems in macroscopic radiation chemistry. It is clear that the higher the value of ϵ, the shorter will be the time before the ion dissociates. At high ionising electron energies, the ions will gain a distribution of excitation energies ϵ up to a maximum, $\epsilon_{\text{max.}}$. Now if it is supposed that, under the conditions of radiation chemistry, competing processes intervene so as to put an upper limit 10^{-q} sec. to the time during which an ion can dissociate, then it follows that only those ions with energies exceeding ϵ_1 will dissociate. On the assumption of a uniform energy distribution, the fraction of ions not dissociating, f_p, is given simply by $\epsilon_1/\epsilon_{\text{max.}}$. The value of $\epsilon_1(q)$ can be calculated from the previous expression by using the known parameters r and s. Stevenson obtained $\epsilon_{\text{max.}}$ by a semi-empirical procedure, and showed that the method was self-consistent with the known mass-spectrum value for f_p when $q = 5$. Stevenson's calculations for f_p when $q = 10$ are shown in Table 2 for a number of dissociation processes; the ϵ_0 values are calculated from the measured ϵ_1 $(q = 5)$. The method undoubtedly gives the correct qualitative trend, but reservations should apply to the use of the theory for small polyatomic molecules and for low ϵ_0 processes.

TABLE 2. *Dissociation of molecular ions.*[35]

	Dissociation	r	s	ϵ_0	$\epsilon_{\text{max.}}$	$f_p(q=5)$	$f_p(q=10)$
Methane	$CH_4^{+\cdot} \rightarrow CH_3^+ + H\cdot$	14	8	1·2eV	2·6eV	0·50	0·85
Ethylene	$C_2H_4^{+\cdot} \rightarrow C_2H_2^{+\cdot} + H_2$	12	11	2·3	6·8	0·44	1·0
Ethane	$C_2H_6^{+\cdot} \rightarrow C_2H_4^{+\cdot} + H_2$	12	17	0·31	4·0	0·13	0·38
n-Hexane	$C_6H_{14}^{+\cdot} \rightarrow C_4H_8^{+\cdot} + C_2H_6$	12	53	0·13	6·3	0·08	0·27
Benzene	$C_6H_6^{+\cdot} \rightarrow C_6H_5^+ + H\cdot$	14	29	2·3	8·1	0·55	1·0

Some conclusions which are pertinent to more condensed systems may now be ascertained. In the gas phase, at atmospheric pressure or thereabouts, ion-molecule reactions or intermolecular energy exchange will begin to intervene for parent ions which are undissociated after 10^{-10} sec., the period between collisions. Hence, f_p corresponding to $q = 10$ is probably a fair guide to the extent of parent-ion dissociation in the usual gas-phase studies.[35] Certainly, no theoretical support can be adduced for the view that the patterns characteristic of mass spectrometry should be reproduced at much higher pressures in gas-phase radiation chemistry. Since the excitation-energy distribution of the ions will be rapidly moderated towards a Maxwell–Boltzmann distribution at high collision frequencies, there is even less likelihood of correspondence between mass patterns and liquid-phase phenomena. On the other hand, these arguments do not deny the existence of ion-dissociation processes in macroscopic radiation chemistry, and it is clear from Table 2 that processes with low ϵ_0 values can be of some importance. Moreover, since the data of Table 2 are only likely to be of qualitative significance for ϵ_0 below 1 ev, the latter conclusion is strengthened by Wolfsberg's contention[33] that rate constants as high as 10^8—10^{10} sec.$^{-1}$, depending on molecule-ion size, obtain even at the threshold for an activation energy of 0·5 ev. To summarise, the dissociation of polyatomic ions along paths of low activation energy should feature prominently in radiation chemistry,[36] on the assumption that ion neutralisation is not the limiting factor.

Among hydrocarbon ions, low ϵ_0 values are mainly encountered in the alkanes where the removal of a bonding electron renders the molecule-ion more susceptible to dissociation. There have been several theoretical papers[37] devoted to the charge distribution in n-alkane molecule-ions, but attempts to predict the most likely point of dissociation in the carbon chain have not proved particularly successful.[38] Experimental information points to the ease with which olefin ions are formed, by loss either of molecular hydrogen or of a lower alkane. Despite the fact that these dissociations involve concerted processes which are expected to have low frequency factors relative to simple bond rupture, the occurrence of olefin ions in the mass spectra of the simple alkanes recorded both at low electron energies,[39] and just above the photoionisation threshold,[40] is especially pronounced. This evidence testifies strongly to the low activation requirements for these four-centre processes. The information with respect to the probability of simple C–H or C–C cleavage of the n-alkane molecule-ions is less clear. It seems that the relative abundances of the various carbonium-ion fragments in mass spectra, which should be a measure of the relative rate constants for all the contributing modes of dissociation, cannot be simply explained in terms of activation-energy differences alone. Enormous variations in frequency factors have to be empirically introduced[39] for processes which are nominally similar, in order to gain formal agreement within the framework of the Eyring theory. In view of this confused situation, no general rule can be stated, but it appears that n-alkane molecule-ions are more prone to rupture at about 2—4 carbon atoms removed from the end of the chain. However, even for the most probable C–C, and certainly for C–H dissociation, the ϵ_0 values are frequently in excess of the requirement for olefin-ion formation.[36]

By contrast, the major dissociation paths for the branched-alkane ions

[36] Ff. Williams, *Trans. Faraday Soc.*, 1961, **57**, 755.
[37] *E.g.*, Lennard-Jones and Hall, *Trans. Faraday Soc.*, 1952, **48**, 581.
[38] Coggeshall, *J. Chem. Phys.*, 1959, **30**, 595.
[39] Friedman, Long, and Wolfsberg, *J. Chem. Phys.*, 1959, **30**, 1605.
[40] Steiner, Giese, and Inghram, *J. Chem. Phys.*, 1961, **34**, 189.

are easily interpretable. It is well recognised that, in the mass spectroscopy of alkanes, branching promotes fragmentation, and that this tendency is particularly prevalent at quaternary substituted carbon atoms. These facts receive an immediate rationalisation in terms of low ϵ_0 values for dissociation at branched sites, irrespective of whether olefin or carbonium ions are formed. Theoretical estimates of ϵ_0 for simple C–C dissociation, which refer to the dissociation energy for the appropriate one-electron bond,[41] are in good agreement with experimental determinations. Since the molecule-ion may be formed with an excess of vibrational energy by electron impact at threshold, negative ϵ_0 values sometimes result from calculations based on electron-impact determinations of ionisation potentials.[36] In such cases, the vibrational energy at threshold presumably exceeds the true ϵ_0 (based on adiabatic ionisation potentials) so that the dissociation is apparently exothermic.

The fact that lower ϵ_0 values obtain for the simple dissociation of branched than of unbranched alkane molecule-ions implies that the difference in thermodynamic stability between the carbonium-ion fragment and the corresponding parent ion is increased by additional alkyl substitution at the electron-deficient carbon atom, as in a comparison of the following dissociation processes for n-butane and 2,2-dimethylbutane:

$$\text{n-}C_4H_{10}^{+\cdot} \rightarrow C_2H_5^+ + C_2H_5\cdot$$
$$(CH_3)_3C\cdot CH_2\cdot CH_3^{+\cdot} \rightarrow (CH_3)_3C^+ + C_2H_5\cdot$$

This result is understandable in terms of the general theorem[42] that hyperconjugation effects due to attached methyl groups operate much more strongly in the even-electron carbonium ion than in the odd-electron parent, so that the dissociation is accompanied by a gain in resonance energy. This gain will obviously be greater, the greater the number of alkyl groups attached to the electron-deficient carbon atom. From the rule that the resonance energy of a carbonium ion exceeds that of the corresponding neutral radical,[43] it follows that the dissociation path naturally tends to favour the formation of the most stable carbonium ion from any particular alkane molecule-ion.

The low ionisation potentials characteristic of unsaturated and aromatic hydrocarbons correspond to the removal of a π-electron from the highest-energy orbital of these compounds. At high ionising electron energies, it is usually considered that any valency-shell electron may be initially detached, but the assumption of rapid internal conversion leads back to the ground electronic state. On a simple picture, it might be supposed that the molecule-ion is not unduly weakened by comparison with the parent molecule, for the orbitals associated with the major binding forces remain intact. If this interpretation is correct, the dissociation of unbranched alkene, and

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[41] Franklin and Lampe, *Trans. Faraday Soc.*, 1961, **57**, 1449.
[42] Cf. Longuet-Higgins, *Chem. Soc. Special Publ.*, 1957, **9**, 5.
[43] Evans, *Discuss. Faraday Soc.*, 1951, **10**, 109.

aromatic, molecule-ions should be characterised by ϵ_0 values akin to the bond dissociation energies found for neutral hydrocarbons (*ca.* 4 ev), rather than by the ϵ_0 values found for the one-electron bonds in alkane molecule-ions, which are often less than 1 ev. This generalisation appears to hold, and it is seen from Table 2 that, in some cases, such high ϵ_0 values militate against any appreciable dissociation of the molecule-ion within the time scale of interest in radiation chemistry.

(b) Ion-molecule Reactions.—The common observation of ions corresponding to a mass = (parent + 1) in the mass spectrometry of hydrogen and its compounds at elevated pressures ($>10^{-5}$ mm.) dates back over thirty years, but it is only since 1952 that detailed attention has been given to the processes responsible for their formation.[44] One of the criteria by which ion-molecule reactions are recognised is a first-order dependence of the ratio of secondary to primary ion current i_{s+}/i_{p+} on the pressure n (molecules per c.c.) in the ion source. In addition, the primary ion is identified unambiguously if i_{p+}/i_{s+} is independent of the ionising electron energy, and if the appearance potentials of the two ions concur. The results from mass spectrometry are conveniently expressed by the equation,

$$i_{s^+} = i_{p^+} n l Q,$$

leading to Q as the phenomenological cross-section[45] for the reaction. Q depends on the "ion-repeller" electric field strength E_r acting on the ion as it traverses a path length l to the exit slit in the ion source. In order to relate Q to the rate constant k for the same reaction when the ions have thermal velocities, a quantity of more general interest in radiation chemistry, it is necessary to outline the theory of ion-molecule reactions.[45]

The short-range interaction of an ion considered as a point charge e acting at a distance r on a polarisable molecule with isotropic electron polarisability α leads to a potential energy $\phi(r) = -e^2\alpha/2r^4$ such that the force $-\partial\phi(r)/\partial r$ between them is attractive. According to Langevin,[46] there exists a critical distance b_0 between the path of the ion relative to the molecule at which they attract to describe a closed capture orbit of initial radius $b_0/\sqrt{2}$. Capture will occur at distances equal to or less than b_0, while interactions beyond b_0 lead only to deflection with approach distance greater than $b_0/\sqrt{2}$. The maximum initial radius of orbital capture $b_0/\sqrt{2}$ corresponds to the distance at which the (attractive) potential energy overcomes the relative kinetic energy of translational motion, and hence b_0 is defined by the equation,

$$\frac{1}{2}\mu g^2 = \frac{e^2\alpha}{2(b_0/\sqrt{2})^4}$$

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[44] Tal'roze and Lyubimova, *Doklady Akad. Nauk. S.S.S.R.*, 1952, **86**, 909; Tal'roze and Frankevich, *ibid.*, 1956, **111**, 376; 1958, **119**, 1174.

[45] Stevenson and Schissler, *J. Chem. Phys.*, 1955, **23**, 1353; 1956, **24**, 926; 1958, **29**, 282; Gioumousis and Stevenson, *ibid.*, 1958, **29**, 294; Stevenson, *J. Phys. Chem.*, 1957, **61**, 1453.

[46] Langevin, *Ann. Chim. Phys.*, 1905, **5**, 245.

where μ is the reduced mass, and g is the relative velocity of the two-particle system. Rearranging, we have

$$b_0^2 = \frac{2e}{g} \cdot (\alpha/\mu)^{1/2},$$

which gives the microscopic capture cross-section, $\sigma(g) = \pi b_0^2$. For $\sigma(g)$ to be equated to the reaction cross-section, it is necessary to assume that the characteristic distance r_c at which the ion and the molecule react with unit probability is less than $b_0/\sqrt{2}$. If this is not the case, reaction could obviously proceed without capture. At very high ion velocities in the mass spectrometer, where $b_0/\sqrt{2}$ (proportional to $g^{-1/2}$) becomes comparable to r_c, it has been shown[47] that the cross-section is reduced to the value based on van der Waals molecular diameters, σ_w. On the other hand, for a Maxwell–Boltzmann distribution of velocities, b_0 will generally exceed r_c, and the rate constant k is given by

$$k = g\sigma(g) = 2\pi e(\alpha/\mu)^{1/2}$$

in terms of fundamental constants for the reacting pair. This expression for k usually exceeds the bimolecular collision number $\pi\sigma_w^2(8kT/\pi\mu)^{1/2}$, by virtue of the large cross-sections at thermal velocities.

It remains to show how k is determined from the mass-spectrometric measurements. When any thermal contributions are neglected, the relative ion velocity g at any point in the ionisation source is determined by the distance x $(0<x<l)$ travelled by the ion of mass m_i from the ionising beam to the exit slit, and is given by

$$\frac{1}{2} m_i g^2 = eE_r x.$$

For the condition $b_0/\sqrt{2} \gg r_c$, and by change of variable, we obtain

$$\sigma(x) = k/g(x) = k(2eE_r x/m_i)^{-1/2};$$

so

$$Q = \frac{1}{l}\int_0^l \sigma(x)dx = k\left[\frac{eE_r l}{2m_i}\right]^{-1/2}.$$

Theory therefore predicts that Q should be proportional to $E_r^{-1/2}$, and this relation holds for many simple reactions involving hydrogen-atom transfer. Substitution of $Q/E_r^{-1/2}$ into the above expression leads directly to k, the fundamental rate constant. It is a spectacular triumph of the theory that the experimentally determined k agrees to better than a factor of two with the predicted value, $2\pi e(\alpha/\mu)^{1/2}$, for reactions and mass-spectrometric conditions which reasonably fulfill the premises on which the theory is based. Thus, for the $(D_2^{+\cdot} + D_2)$ reaction, $k_{\text{calc.}}$ is $8{\cdot}7 \times 10^{11}$ l. mole^{-1} sec.$^{-1}$, to be compared with $k_{\text{exp.}} = 8{\cdot}6 \times 10^{11}$ l. mole^{-1} sec.$^{-1}$. Excellent agreement also obtains for the $(Ar^{+\cdot} + H_2)$ reaction. It is true that more

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[47] Boelrijk and Hamill, *J. Amer. Chem. Soc.*, 1962, **84**, 730.

complicated reactions cannot be treated by this simple theory, and that the linear dependence of Q on $E_r^{-1/2}$ is often not obeyed, but the general conclusion remains that the rates of all ion-molecule reactions observed in the mass spectrometer are so large that there is a high probability, η, of reaction upon every encounter. No theoretical predictions of η have been made, but it seems clear from experiment that there is often no dependence on temperature; in other words, these observed reactions have no activation energy in the usual sense. This conclusion leads to a most useful corollary, namely, that ion-molecule reactions must surely be exothermic. Where independent thermochemical data are available to check this statement, it has been found to hold true. This principle has been used by Tal'roze *et al.*[44] to establish limits for thermochemical quantities. Thus, for the proton-transfer reaction,

$$RH^{+\cdot} + M \rightarrow R\cdot + MH^{+}$$

the criterion for exothermicity can be expressed in the form,

$$P_M + I_{RH} > D_{H-R} + I_H,$$

where P_M is the proton affinity of M, I_{RH} and I_H are the ionisation potentials of RH and the hydrogen atom, respectively, and D_{H-R} is the appropriate bond dissociation energy. If the reaction is observable, a lower limit to P_M may be readily assigned on the basis of the known values for the other quantities. Tal'roze *et al.* further suggest that if a reaction is not observed for a particular RH, then the inequality sign in the thermochemical equation can be reversed so as to establish an upper limit to P_M. By suitable variation of RH, P_M may thus be defined within close limits. However, this procedure of obtaining the upper limit for P_M implies that exothermicity is a sufficient condition for the observation of an ion-molecule reaction. This criterion cannot be rigorously applied, for ion-molecule reactions with rate constants less than 10^9 l. mole^{-1} sec.$^{-1}$ would probably not be detected, although many such reactions could still be exothermic. The observation of a particular ion-molecule reaction might also be prevented by a more favourable competing reaction or by simple charge transfer.

The analogy between the reactions of odd-electron ions and free radicals is brought out clearly by the process of hydrogen-atom transfer,

$$X^{+\cdot} + R{-}H \rightarrow X{-}H^{+} + R\cdot$$

This type of reaction often occurs only where the parent atom or molecule X has at least one lone pair of electrons (*e.g.*, Ar, H_2O, NH_3) or π-electrons (*e.g.*, olefins), so that the secondary ion XH^+ represents the corresponding X-onium ion; interesting exceptions are methane and hydrogen. In principle, the neutral molecule RH may be almost any hydrogen-atom donor, subject to the exothermicity rule. Another important reaction of odd-electron ions is proton transfer from the ion to a neutral molecule, where the latter has intrinsic basicity. In this manner, alkane ions can become neutral free radicals, *e.g.*,

$$C_3H_8^{+\cdot} + H_2O \rightarrow C_3H_7\cdot + H_3O^+$$

When a reaction occurs between an olefin ion and the same neutral olefin, *e.g.*,

$$C_3H_6^{+\cdot} + C_3H_6 \rightarrow C_3H_7^+ + C_3H_5\cdot$$

then the mechanism may involve hydrogen atom or proton transfer. In both these reactions, the primary odd-electron ion is replaced by a secondary even-electron ion, and the greater stability of the latter contributes a powerful driving force. Other reactions of odd-electron ions are known in which the net transfer of several atoms takes place. Here, the reaction appears to proceed through an activated collision-complex. In the reaction of the ethylene molecule-ion with ethylene,[4] the products were found to be strikingly similar to those obtained in the ordinary mass spectrum of the butenes, suggesting that intimate "ion-molecule condensation" occurs to form an excited species akin to a butene molecule-ion before fragmentation:

$$C_2H_4^{+\cdot} + C_2H_4 \rightarrow [C_4H_8^{+\cdot}] \rightarrow C_3H_5^+ + CH_3\cdot$$

The reactions of even-electron positive ions are, of course, well known in conventional chemistry, where carbonium ions are postulated as intermediates in many organic reactions.[48] In the gas phase, the main type of reaction observed is hydride-ion transfer from a hydrocarbon resulting in a more stable even-electron ion. Exothermicity implies a lower bond-heterolysis energy for the formation of the product ion, relative to the initial ion, from their respective hydrocarbons. An example is the reaction of the fragment ion $C_3H_5^+$ with neopentane,[4] *viz.*,

$$C_3H_5^+ + \text{neo-}C_5H_{12} \rightarrow C_3H_6 + C_5H_{11}^+$$

It is relevant to mention that mass-spectrometric conditions do not altogether favour the study of carbonium-ion reactions. First, these species are only formed in secondary processes which makes subsequent observations less certain; and, secondly, many of their reactions are probably characterised by rate constants less than 10^9 l. mole^{-1} sec.$^{-1}$, and therefore lie outside the range of detection. It is clear that the detailed nature of secondary processes cannot be inferred on the basis of mass-spectroscopic studies alone.

(c) **The Neutralization of Ions.**—Only a meagre amount of reliable quantitative information is available on this important subject. Theoretical considerations[49] suggest that the neutralisation of polyatomic ions by electrons occurs largely through dissociative recombination. In accordance

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[48] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953.

[49] Massey and Burhop, "Electronic and Ionic Impact Phenomena," Clarendon Press, Oxford, 1952, pp. 225. 631.

with the Franck–Condon principle, thermal electron capture proceeds non-adiabatically by a crossing of potential-energy surfaces without change in nuclear positions, so that the initial Coulombic energy between the charges is conserved in the energy associated with the electronic state of the products. Since the product configuration will often be formed on a repulsive potential-energy surface, dissociation is the likely outcome. Here, as before, it is important to dwell on the essential difference between odd- and even-electron ions. The parent molecule-ion can recapture an electron to form an electronically excited molecule, which may or may not undergo subsequent dissociation. Even-electron ions of the type represented by H_3^+, H_3O^+, NH_4^+ must surely undergo dissociation on neutralisation with the probable formation of a hydrogen atom and the neutral molecule. The possibilities for the carbonium-ion discharge are two-fold: either dissociation to form the corresponding olefin and the hydrogen atom, or the formation of a free radical.[36]

One of the most crucial questions in radiation chemistry concerns the mean lifetime of ions under ordinary conditions of irradiation. It has been argued[45] that, if the measured recombination coefficients[49] for diatomic noble-gas ions (*e.g.*, $Ar_2^{+\cdot}$) also apply to polyatomic ions, then the lifetime of the latter is easily sufficient to allow ion-molecule and ion-dissociation processes to compete with neutralisation in the gas phase. In liquids, electron capture has often been assumed to be almost instantaneous after the ionisation event, with little chance for ionic reactions; a justification for this view is the approximate calculation[20] that electrons rapidly lose their excess energy in liquids within range of the strong Coulombic force between the parent ion and the electron. More recently, direct chemical evidence for ionic reactions in the liquid phase has forced a reconsideration of the matter. Since it is now generally recognised[50] that ion-molecule reactions can proceed in the liquid phase, the subsequent neutralisation will often involve an even-electron ion. In the last connection, the Franck–Condon principle may be more restrictive than in the case of parent-ion neutralisation. Studies of the mechanism of electron-transfer[51] and of the discharge of ions at electrodes in solution[52] suggest the need for the ion to assume the correct configurational requirement before electron transfer, and that this requires a vibrational energy of activation. If these conclusions apply also to even-electron ions in radiation chemistry, then Coulombic attraction is not a sufficient condition for discharge, and a slow thermal activation process could be the limiting factor. For odd-electron ions, these considerations break down because of the strong spin coupling between the free valency of the ion and the electron; indeed, it was remarked long ago that thermal electron capture is always most favoured by molecules with free valencies.[10]

[50] Magee, *Ann. Rev. Phys. Chem.*, 1961, 389.
[51] Halpern, *Quart. Rev.*, 1961, **15**, 207.
[52] Gurney, *Proc. Roy. Soc.*, 1931, *A*, **134**, 137.

The probability of negative-ion formation by electron attachment to neutral molecules depends on the incident electron energy. Negative ions are often formed through dissociative resonance capture,[49] but the ability to take up thermal electrons is limited to a relatively small number of molecules including oxygen, some alkyl halides, and several aromatic compounds. These conclusions rest upon direct measurements in the gas phase, and, in the case of aromatic compounds, on negative-ion formation in solutions, where the electron donor can be either an alkali metal or a metal electrode. Recently, electron attachment to naphthalene in solid solutions has been observed[53] to follow γ-ray irradiation at $-196°$ (identification of the negative ion-radical was based upon its characteristic absorption spectrum). Very few reactions of negative ions with molecules have been detected,[4] and none of these involves hydrocarbon ions. It is often tacitly assumed that an electron-capture process in either the gas or the liquid phase necessarily prolongs the life of the positive ion; such a generalisation appears to be ill-founded, for the recombination coefficients for ion–ion neutralisation are of the same order of magnitude as for the ion–electron process in the gas phase.[54] Moreover, if the transfer of an electron from a negative ion to an even-electron positive ion is limited by Franck–Condon restrictions, then an alternative process of a proton transfer from an X-onium ion to the negative ion could be more favourable, *viz.*,

$$XH^+ + Y^- \rightarrow X + HY$$

(d) Electronic Excitation Processes.—The contribution of the electronically excited states of neutral molecules in radiation chemistry is difficult to assess. In principle, the possible processes affecting excited states are numerous. On the physical side, the excitation energy can sometimes be transferred selectively over long distances, light emission may occur, or the energy is simply degraded to internal energy. From a chemical standpoint, the excited state—singlet or triplet—can undergo direct reaction or decompose to give free radicals. Unfortunately, no predictive power is available over this gamut of possibilities. Even analogies with known photochemical behaviour are not always too helpful, because the nature of the excited states must often differ in the two instances. However, *a posteriori*, excited states are seen to flourish in many mechanisms of radiation action. A more fundamental approach is due to Burton and his school,[55] who have sought to establish whether the factors affecting short luminescence-decay times also influence the chemical changes. It appears certain that the longer-lived states responsible for much of the fluorescence shown by aromatic compounds are unconnected with the chemical action.

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[53] Rao, Nash, Guarino, Ronayne, and Hamill, *J. Amer. Chem. Soc.*, 1962, **84**, 500.

[54] Loeb, "Basic Processes of Gaseous Electronics," Univ. of California Press, Berkeley, 1955, pp. 556, 577.

[55] Burton and Lipsky, *J. Phys. Chem.*, 1957, **61**, 1461; Burton and Dreeskamp, *Discuss. Faraday Soc.*, 1959, **27**, 64.

4. Macroscopic Radiation Chemistry

Most of the experimental work in radiation chemistry relates to the measurement of overall chemical change. In recent years, two techniques have been used for the direct identification of transient intermediates. First, pulse radiolysis can be applied, and the absorption spectra of the transients determined as in the flash-photolysis method;[56] this approach has met with some success in the radiolysis of aromatic compounds.[57] Secondly, free radicals have been identified during the radiolysis of liquid alkanes at low temperature by measurement of electron-spin resonance.[58] In favourable cases, both techniques allow kinetic studies leading to the determination of absolute rate constants. These methods are generally limited to intermediates with mean lifetimes in excess of 10^{-6} sec., and therefore supply information about the nature and chronology of the secondary free-radical processes subsequent to the elementary reactions. Since the detailed nature of free-radical interactions can only be inferred from conventional chemical studies, a further extension in the use of direct methods is desirable and should help to bridge the gap between the primary processes and the overall results.

(a) Reactions in the Gas Phase.—Although it lies outside the title of this Review, the radiation-induced exchange between hydrogen and deuterium[59] is of particular interest. The importance of this work lies in the finding that the reaction is dominated by proton or deuteron exchange between secondary ions of the H_3^+ type and molecular hydrogen in various isotopic forms, *e.g.*,

$$H_3^+ + D_2 \rightarrow H_2 + HD_2^+$$

Convincing evidence for this conclusion is the thousand-fold reduction in HD yield on the addition of krypton or xenon in small quantities to the system. These noble gases have no effect on the photosensitised exchange induced by hydrogen atoms, and their inhibitory action on the radiation-induced process is ascribed to their having proton affinities higher than that of molecular H_2, $P_{Kr} > 93$ kcal./mole, which allows the chain-breaking reaction

$$H_3^+ + Kr \rightarrow H_2 + KrH^+$$

to compete successfully with the above propagation step. The high ion-pair yield ($M/N = 18{,}000$) for HD formation in the absence of inhibitors reflects the ease with which the H_3^+ ions formed in the primary ion-molecule encounters can undergo successive proton transfers before neutralisation. It is interesting that in some independent work[54] the rate of ion–electron recombination in very pure hydrogen has been found to be very low

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[56] Porter, *Proc. Roy. Soc.*, 1950, *A*, **200**, 284.
[57] McCarthy and MacLachlan, *Trans. Faraday Soc.*, 1960, **56**, 1187.
[58] Fessenden and Schuler, *J. Chem. Phys.*, 1960, **33**, 935.
[59] Thompson and Schaeffer, *J. Amer. Chem. Soc.*, 1958, **80**, 553; *Radiation Res.*, 1959, **10**, 671.

but that the ions disappear rapidly in the presence of impurities (H_2O, O_2) which are able to form negative ions. The most reasonable explanation is ready proton transfer to the negative ion, as discussed above.

Two ion-molecule reactions have been observed for methane, *viz.*:

$$CH_4^{+\cdot} + CH_4 \rightarrow CH_5^+ + CH_3\cdot$$
$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

Analogous reactions have not been observed for the other alkanes; this may be due to lower cross-sections, but the cause could lie deeper. In order for hydrogen-atom transfer to occur from a neutral molecule to its molecule-ion, the exothermic criterion can be written

$$I_{RH} + P_{RH} > I_H + D_{R-H}$$

With increase in alkane size, I_{RH} decreases significantly (Table 1) in comparison with change in the C–H bond-dissociation energy, D_{R-H}. Thus, except in the unlikely event that P_{RH} increases with alkane size, the first reaction would become energetically less favourable for the higher alkanes. The second reaction leading to the $C_2H_5^+$ ion may also be specific, for a general process of this type is unknown among carbonium-ion reactions in organic chemistry. The experimental work on the radiation chemistry of methane has led to some conflict of interpretation. Lampe,[60] using 1·7 Mev electrons, has obtained results in good agreement with previous α-ray work by Lind and Bardwell (cf. ref. 7); methane disappears with a *G*-value of 5·7, and hydrogen, ethane, ethylene, and propane are formed with *G*-values of 5·7, 2·1, 0·05, and 0·14, respectively. The formation of propane as a primary product, and the independence of the initial yields on pressure and irradiation intensity, have been interpreted[60] in terms of the previous ion-molecule reactions which would lead to the direct formation of a C_2 intermediate. However, it has been shown that the product distribution is almost identical in the mercury-photosensitised photolysis,[61] and R. R. Williams[62] has also obtained similar results using a swarm of low-energy electrons, irrespective of the applied voltage. Better evidence for ionic processes comes from the radiolysis of argon–methane mixtures;[63] the results could be quantitatively interpreted in terms of the dissociative charge-transfer reaction,

$$Ar^{+\cdot} + CH_4 \rightarrow Ar + CH_3^+ + H\cdot$$

and the subsequent reaction of the CH_3^+ ion to form molecular hydrogen. Recently,[64] attention has been directed to the "missing" products which must account for the lack of C/H material balance in the products of low molecular weight from the radiolysis of methane; at high (*ca.* 30%) conversions, hydrocarbons between C_{14} and C_{18} have been detected.[64]

[60] Lampe, *J. Amer. Chem. Soc.*, 1957, **79**, 1055; *Nucleonics*, 1960, **18**, 60.
[61] Mains and Newton, *J. Phys. Chem.*, 1961, **65**, 212.
[62] R. R. Williams, jun., *J. Phys. Chem.*, 1959, **63**, 776; 1962, **66**, 372.
[63] Meisels, Hamill, and R. R. Williams, jun., *J. Phys. Chem.*, 1957, **61**, 1456.
[64] Hummel, *Nature*, 1961, **192**, 1178.

The radiolysis of ethane at low conversion[65] leads to the formation of hydrogen, methane, ethylene, and n-butane with *G*-values of 8·8, 0·39, *ca.* 2·0, and 2·5, respectively. In a valuable contribution, Dorfman[66] has shown that a significant part of the hydrogen and methane yields are due to "molecular" processes, which are defined as proceeding without atom or radical precursors. This conclusion is securely based on the isotopic distribution of the products obtained from the irradiation of C_2H_6–C_2D_6 mixtures, and also on the dimunition in total yields when ethylene or propene is present in sufficient amount (*ca.* 2 mole %) to act as a scavenger for the intermediate atoms and radicals. In many cases, these molecular processes may be plausibly ascribed to parent-ion fragmentation and ion-molecule reactions. For example, the following processes may apply for ethane:

$$C_2H_6^{+\cdot} \rightarrow C_2H_4^{+\cdot} + H_2$$
$$C_2H_3^{+} + C_2H_6 \rightarrow C_3H_5^{+} + CH_4$$

The yields are often found to be quantitatively consistent with an assessment of contributing ionic processes,[66] but the agreement may be partly fortuitous in view of uncertainties regarding the choice of fragmentation pattern, and the possible contribution of excited-molecule precursors.[67]

The reactions of an ostensible free-radical scavenger may be complicated if it has a low ionisation potential (cf. NO) or electron affinity, or if it can react with the ionic precursors; conclusions derived from the use of many so-called scavengers have to be carefully examined. However, there is good circumstantial evidence that hydrogen atoms are formed as intermediates in the radiolysis of ethane, propane, and, presumably, the higher n-alkanes. A careful study[68] has shown that unsaturated compounds are primary products in the radiolysis of n-alkanes and that, even at low conversion, these compounds are effective as internal scavengers in reducing the yield of hydrogen gas from the initial yield to a constant value characteristic of a steady-state concentration of unsaturated hydrocarbons in the system. The variation in the yield of hydrogen gas with the concentration of unsaturated components obeys a kinetic relationship based on the assumptions that hydrogen atoms are formed and react competitively by abstraction and addition; the ratios of rate constants for these reactions agree closely with those obtained in comparative studies of mercury-photosensitised decomposition.[68] This approach has been extended to the temperature-dependence of propane radiolysis;[69] the results comply with Arrhenius expressions for the rate constants, and the absolute parameters are

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[65] K. Yang and Gant, *J. Phys., Chem.*, 1961, **65**, 1861.

[66] Dorfman, *J. Phys. Chem.*, 1958, **62**, 29; Dorfman and Sauer, jun., *J. Chem. Phys.*, 1960, **32**, 1886; *J. Phys. Chem.*, 1962, **66**, 322.

[67] Okabe and McNesby, *J. Chem. Phys.*, 1961, **34**, 668; 1962, **36**, 601.

[68] Back and N. Miller, *Trans. Faraday Soc.*, 1959, **55**, 911; Back, *J. Phys. Chem.*, 1960, **64**, 124.

[69] K. Yang, *J. Amer. Chem. Soc.*, 1962, **84**, 719.

derived by normalisation to an assumed rate constant for one of the reactions. Agreement with independent values is somewhat less than satisfactory, but the internal consistency of the method is encouraging.

An attempt has been made[70] to account for some of the radiolysis products from n-hexane in terms of a detailed reaction mechanism. First, it is assumed that the fragmentation pattern from mass spectra is applicable. Secondly, all exothermic hydride-ion transfer reactions are allowed between fragment ions and n-hexane. Finally, the $C_6H_{13}^+$ ion is taken to be neutralised to form C_6H_{12} olefins and atomic hydrogen, the latter undergoing subsequent abstraction to form H_2 and $C_6H_{13}\cdot$. All radicals are assumed to disappear by combination and disproportionation in accordance with the known rate constants for these reactions. This treatment accounts for the products below C_6 with satisfactory precision. In some later work,[71] the yields of C_6 products have been found to be extremely small, and this seems to be at variance with part of the above mechanism.

Neopentane[60] and isobutane[68] give larger yields of methane than are obtained from the corresponding n-alkanes. This result is completely consistent with the preferred unimolecular decomposition of the branched parent-ions to give methane and methyl radicals. Gevantman and R. R. Williams[72] have noted that the radioactive distribution of alkyl iodides formed by the radiolysis of alkanes in the presence of iodine-131 bears a complementary relationship to the mass spectrum of the alkane in some cases; this correspondence is especially striking for neopentane, where methyl iodide is by far the most prominent product.

To summarise, it is apparent that consideration of the possible dissociation paths of the alkane parent-ion, and of the ion-molecule reactions of fragment ions, serves as a useful guide in accounting for product distribution. However, the origin of atomic and molecular hydrogen has not been established; hydrogen atoms could arise from dissociation of the parent ion, from neutralisation of the parent or secondary ions, or from non-ionic precursors. Also, undetected hydrocarbons of higher molecular weights must invariably be formed to balance the poor C/H material balance in the sum of identified products, especially where substantial conversions of the starting material are effected. Whether these unknown hydrocarbons are formed through radical or ionic polymerisation of olefinic products, or even by some sort of direct ion–molecule condensation, remains unresolved; the work of Back and N. Miller[68] at low conversions indicates that unsaturated compounds play a most important role in secondary reactions.

The most general reaction undergone by unsaturated compounds is polymerisation. At atmospheric pressure or thereabouts, the chain lengths are usually short, and rarely do the ion-pair yields or the molecular weights

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[70] Futrell, *J. Amer. Chem. Soc.*, 1959, **81**, 5921.

[71] Dewhurst, *J. Amer. Chem. Soc.*, 1961, **83**, 1050.

[72] Gevantman and R. R. Williams, jun., *J. Phys. Chem.*, 1952, **56**, 569.

of the resultant polymers correspond to a degree of polymerisation exceeding 100 monomer units;[7] the latter value has been reported for isobutene vapour at 0°. The ion-pair yields for a variety of unsaturated compounds[7] show that 4—10 monomer molecules disappear but that, on the average, the combined yield of hydrogen and methane is less than unity. These results conform to the interpretation that dissociation of the parent ion assumes much less importance for unsaturated than for saturated hydrocarbons. The most detailed studies have been made on acetylene and ethylene. Acetylene polymerizes to form a highly cross-linked material, cuprene, with an ion-pair yield, $-M/N = 16$; a smaller conversion $(-M/N \sim 4)$ of acetylene to benzene is also obtained, but at low pressures ($<$ 20 mm.) the yield of benzene decreases whereas cuprene formation is unaffected. It is thought[73] that these reactions involve different mechanisms, and that benzene is formed through excited molecules which become deactivated on the walls at low pressure. Almost no hydrogen is formed by the direct radiolysis of acetylene. Ions identified in the α-ray mass spectometer[23] at pressures up to 0·1 mm. of acetylene include $C_4H_2^+$, $C_4H_3^+$, $C_6H_4^+$, and $C_6H_5^+$ as products of ion–molecule reactions. The low intensity of $C_4H_4^+$ could be explained by supposing that simple ion–molecule addition leads to an excited product ion which readily dissociates under low-pressure conditions.

An interesting feature of acetylene polymerisation is the reproducibility of the yield, even in the presence of many added gases. Lind's original suggestion of ion-molecule clusters has now been confirmed[74] by direct observation of ionic xenon–acetylene complexes in the high-pressure mass spectrometer, but the detailed mechanism of polymerisation at atmospheric pressure is still obscure.[7] Compared with acetylene, the polymerisation yield from ethylene is more variable with pressure. Irradiation under high pressures (*ca.* 100 atm.) leads to a high yield of solid polymer, but at pressures close to atmospheric the ion-pair yield for ethylene disappearance is *ca.* 5·1 $[G(-C_2H_4) = 18]$, suggesting only a low degree of polymerisation. All the products up to C_6 compounds account for less than a third of the ethylene which reacts; hydrogen and acetylene are the main gaseous products with *G*-yields of 1·2 and 2·4, respectively, but below 150 mm. pressure these yields increase significantly.[66] Ionic processes for hydrogen and acetylene formation depend upon the fragmentation of the parent ion, but Stevenson's calculations (Table 2) suggest that the competing ion–molecule reaction between $C_2H_4^{+\cdot}$ and C_2H_4 would be strongly favoured. At pressures between 7 and 20 atm., both acetylene and ethylene undergo alkylation with propane;[75] the *G*-values for conversion range up to 100 and it has been argued that free-radical chains are probably involved.

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[73] Dorfman and Wahl, *Radiation Res.*, 1959, **10**, 680.
[74] Rudolph, Lind, and Melton, *J. Chem. Phys.*, 1962, **36**, 1031.
[75] Bartok and Lucchesi, *J. Amer. Chem. Soc.*, 1959, **81**, 5918; 1960, **82**, 4525.

The radiolysis of benzene vapour[76] gives low *G*-yields of acetylene (0·11), ethylene (0·05), and hydrogen (0·01), but *G* for disappearance[7] to "polymer" is 4·9. The tendency for aromatic hydrocarbons to form involatile residues is less than that shown by unsaturated compounds, but a high ratio of "polymer" to gas products is common to both groups. By the Wilzbach exposure method, tritium is incorporated into benzene vapour[77] with *G*-yields from 0·11 to 0·35, whereas corresponding values for hexane and cyclohexane are less than 0·02. The labelling cannot be due to the capture of recoil tritons and is probably caused by the reaction of ionised or excited benzene molecules with the tritium gas.

(b) Reactions in the Liquid Phase.—Although there is good experimental agreement as to the general pattern of results, considerable doubt often surrounds the finer mechanistic details. This situation results from the uncertainty regarding the precise action of additives which are used as probes for the intermediate species.

(*i*) *Alkanes.* Relative to the gas-phase results, the radiolysis of liquid n-hexane shows about the same yield of total products but the distribution is characterised by much less C–C bond scission and by more dimerisation.[78] The *G*-yield of hydrogen gas from liquid n-alkanes is almost invariant with chain length, being 4·1 for n-pentane,[79] 5·0 for n-hexane,[78] and 6·0 for linear polyethylene.[80] Branched alkanes, including polymers, are less prone to dimerise than n-alkanes but undergo cleavage in the main chain at the most substituted carbon atom, irrespective of phase conditions. The C–C bond rupture in n-pentane, although much less evident than for branched alkanes,[78] leads mainly to C_2 and C_3 intermediates, as reflected in the product distribution.[79] These results on C–C fragmentation parallel the ease with which the parent molecule-ion dissociates in the various positions. For the higher n-alkanes extending up to linear polyethylene, the amount of chain scission is small compared with that of dimerisation (cross-linking). The probability that the small amount of C–C cleavage in the liquid n-alkanes occurs most readily near the ends of the chain is not inconsistent with the finding that virtually no C–C scission occurs in cyclohexane.[81]

As in the gas phase, olefins are formed and subsequently interfere in secondary processes. The major olefinic products from the n-alkanes are of the same carbon number, whereas branched alkanes give rise to olefins by fragmentation. We have seen that olefin ions can be readily formed by

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[76] Manion and Burton, *J. Phys. Chem.*, 1952, **56**, 560.

[77] Riesz and Wilzbach, *J. Phys. Chem.*, 1958, **62**, 6.

[78] Dewhurst, *J. Phys. Chem.*, 1958, **62**, 15; *J. Amer. Chem. Soc.*, 1958, **80**, 5607; Holroyd, *J. Phys. Chem.*, 1961, **65**, 1352.

[79] Wagner, *J. Phys. Chem.*, 1960, **64**, 231.

[80] Ff. Williams and Dole, *J. Amer. Chem. Soc.*, 1959, **81**, 2919.

[81] Dyne and Jenkinson, *Canad. J. Chem.*, 1960, **38**, 539; 1961, **39**, 2163; Dyne and Fletcher, *ibid.*, p. 851; Dyne and Stone, *ibid.*, 1961, **39**, 2381; Dyne, Jenkinson, and Denhartog, A.E.C.L. 1416 (Chalk River, Ontario).

low-energy paths from the parent ion, but a previous suggestion[36] that the olefinic products arise by this route must be re-examined. In the first place, the olefin ion may react further before neutralisation; a possible ion–molecule reaction is hydrogen-atom abstraction to form a carbonium ion, although subsequent neutralisation of the latter would probably give the olefin and a hydrogen atom. A more serious objection is that in low-voltage mass spectra,[39] olefin ions corresponding to the loss of molecular hydrogen from the higher n-alkanes appear only with very low intensities. However, chemical evidence shows that typical free-radical scavengers, other than oxygen, do not seriously affect the olefin yield so that the process is certainly "molecular".

The major products from cyclohexane are hydrogen ($G = 5{\cdot}6$), cyclohexene ($G = 3{\cdot}3$), and bicyclohexyl ($G = 2{\cdot}0$);[81] the simplicity of the overall reaction, and the attainment of a good material balance, has prompted a number of detailed studies. The simplest interpretation of the results obtained with added iodine[82] is that thermal hydrogen atoms are captured, to form hydrogen iodide ($G = 2{\cdot}0$), that cyclohexyl radicals react to give cyclohexyl iodide ($G = 3{\cdot}7$), and that the balance between these two yields is due to some primary process in which the hydrogen is unscavengeable (*i.e.*, molecular), cyclohexyl radicals being formed as represented by the empirical equation,

$$\text{cyclo-}C_6H_{12}^* + \text{cyclo-}C_6H_{12} \rightarrow 2\text{cyclo-}C_6H_{11}\cdot + H_2$$

This process could involve translationally "hot" hydrogen atoms from some unknown precursor, or any bimolecular reaction of an excited or ionised species. The depression of the hydrogen gas yield ($-\Delta G = 2{\cdot}0$) by the addition of iodine is equivalent to the amount of hydrogen iodide formed, and is consistent with the above results on the reasonable assumption that, in the absence of iodine, thermal hydrogen atoms abstract hydrogen from cyclohexane to form H_2 and cyclohexyl radicals. Clear evidence for the role of intermediate cyclohexyl radicals is the demonstration[83] that 2,5-dicyclohexylquinol, and 2,5-dicyclohexyl-1,4-benzoquinone are formed to the exclusion of bicyclohexyl when benzoquinone is used as a scavenger. Some authors persist in regarding cyclohexene as a product of radical disproportionation, but the fact that the cyclohexene yield is virtually unaffected by benzoquinone,[83] and only slightly reduced by iodine,[82] would then imply that the radical precursors of cyclohexene differ from those of bicyclohexyl in being unscavengeable. The importance of radical disproportionation in the liquid state has also been questioned by others,[79] and it seems better to regard most of the olefin formation as due to a molecular process. In a novel approach to the problem of the origin of molecular hydrogen, Dyne and his co-workers[81] have studied the initial yield of D_2 from dilute solutions of cyclo-C_6D_{12} in cyclo-C_6H_{12}. By

[82] Forrestal and Hamill, *J. Amer. Chem. Soc.*, 1961, **83**, 1535.
[83] Waight and P. Walker, *J.*, 1960, 2225.

extrapolating the G-yield of D_2, calculated on the basis of the energy absorbed only by the cyclo-C_6D_{12}, to infinite dilution, the "first-order" G-yield of D_2 originating from separated cyclo-C_6D_{12} molecules is found to be 0·25. This value is much lower than the molecular yield[82] ($G = 3·9$) of hydrogen from cyclo-C_6H_{12}, but even more interesting is the fact that this "first-order" yield is not characteristic of cyclo-C_6D_{12} alone but depends on the diluent; for example, this yield is about eight times greater in n-hexane than in cyclohexane. Moreover, the "first-order" yield in cyclohexane is affected by added iodine and benzene. Thus, even that fraction of hydrogen which appears experimentally to be "unimolecular" is a function of molecular environment!

The cyclohexane–benzene system has attracted considerable interest since Manion and Burton[76] showed that the product yields, especially of hydrogen gas, do not obey the simple additive rule that would apply if each component absorbed energy in proportion to its electron fraction and then decomposed independently of the other. In the original paper,[76] it was argued that the effect could not be completely explained in terms of hydrogen-atom scavenging by the benzene, and that excitation and/or charge-transfer operate whereby the benzene "protects" the cyclohexane from decomposition. Freeman[84] has carried out a kinetic study and concludes that benzene acts both as a hydrogen-atom scavenger, and as a recipient of energy transfer; two types of excited (or ionised) cyclohexane species are suggested. A more revolutionary idea[85] is that the effect may be simply a matter of energy absorption, this being determined, not by the respective electron fractions of the components, but by a more complicated relation based on oscillator strengths for the ultraviolet absorption bands.

On the assumption that added solutes (olefins, alcohols, and halogen compounds) affect the hydrogen-gas yield on radiolysis of n-hexane and other alkanes by reacting with intermediate hydrogen atoms, Hardwick[86] has developed a method similar to that used in gas-phase radiolysis[68] to obtain quantitative comparisons of the rate constants for abstraction and addition processes involving hydrogen atoms. A good correlation is obtained with existing data for the same reactions in the gas phase, where the hydrogen atoms originate from thermal or photochemical sources. The results on temperature-variation of the radiolysis reactions are less easy to interpret in the conventional manner.

(*ii*) *Unsaturated hydrocarbons.* A new light has been thrown on the condensation reactions of alkenes by the finding[87] that 90% of the dimeric product from the radiolysis of hex-1-ene consists of a monoolefin. Only diolefinic dimers are formed by the known free-radical-induced reactions

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[84] Freeman, *J. Chem. Phys.*, 1960, **33**, 71.
[85] Lamborn and Swallow, *J. Phys. Chem.*, 1961, **65**, 920.
[86] Hardwick, *J. Phys. Chem.*, 1960, **64**, 1623; 1961, **65**, 101; 1962, **66**, 117, 291.
[87] Chang, N. C. Yang, and Wagner, *J. Amer. Chem. Soc.*, 1959, **81**, 2060.

of terminal olefins. The carbon skeleton of the radiation-induced dimer from hex-1-ene is thought[87] to arise from the union of a molecule-ion with a molecule, formally analogous to the reaction of the ethylene molecule-ion in the mass spectrometer, except that the dimer ion is assumed to be less prone to dissociate in the liquid phase and then becomes neutralised to form the monoolefinic structure. This work[87] also reveals a low yield of hydrogen gas ($G = 0{\cdot}9$) and the virtual absence of C–C fragmentation in hex-1-ene. Strong support for the predominant role of ionic processes in the radiation chemistry of terminal olefins also comes from a study of n-hexadec-1-ene;[88] the product pattern, and the minor effects caused by radical scavengers, could not be reconciled with a free-radical mechanism. The radiolysis of propene[87] and 2,4,4-trimethylpent-1-ene[89] again lead to higher mono-olefins, amongst other products, but it is noteworthy that cyclohexene[90] is reported to give a larger yield of bicyclohexenyl ($G = 1{\cdot}36$) than of the mono-olefin, cyclohexylcyclohexene ($G = 0{\cdot}2$). Irradiation of (+)-α-pinene[91] leads to racemisation and isomerisation, in addition to formation of low molecular weight polymers (average, trimer). In most of these studies, the reported G-yields for the disappearance of olefin do not exceed 20, so any secondary initiation of the short-chain polymerisation by transfer must be of low probability.

By comparison with the above, most of the work on the radiation-induced polymerisation of vinyl monomers has been interpreted in terms of free-radical reactions. This is not surprising, for even a low yield of free radicals is sufficient to cause appreciable polymerisation if the monomer is susceptible to this mode of initiation. Evidence that a radical mechanism operates in many cases comes from the dependence of the polymerisation rate on the square root of the dose rate up to a limiting value of the latter, and also from the agreement in the yield of initiators deduced from polymerisation kinetics with determinations based on the use of radical scavengers.[92] Free-radical initiation is also inferred from the formation of a 1:1 copolymer in the irradiation of an equimolar styrene–methyl methacrylate mixture,[93] whereas conventional cationic and anionic initiators give homopolymers of styrene and methyl methacrylate, respectively, from the same mixture. At one time, available evidence suggested the absence of ionic initiation by irradiation, but this generalisation is no longer valid. For example, monomers which polymerise readily by a cationic mechanism but not by free-radical initiation have also been polymerised by irradiation; these include isobutene[94,95] at −78°, α-

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[88] Collinson, Dainton, and D. C. Walker, *Trans. Faraday Soc.*, 1961, **57**, 1732.

[89] de Gorski and de Gaudemaris, *Compt. rend.*, 1959, **248**, 969; 1959, **249**, 421.

[90] Freeman, *Canad. J. Chem.*, 1960, **38**, 1043.

[91] Bates, Best, and Ff. Williams, *J.*, 1962, 1521.

[92] Chapiro and Magat, "Actions Chimiques et Biologiques des Radiations," Masson et Cie., Paris, 1958, Vol. III.

[93] Seitzer, Goeckermann, and Tobolsky, *J. Amer. Chem. Soc.*, 1953, **75**, 755.

[94] Davison, Pinner, and Worrall, *Proc. Roy. Soc.*, 1959, *A*, **252**, 187.

[95] Collinson, Dainton, and Gillis, *J. Phys. Chem.*, 1959, **63**, 909.

methylstyrene,[96] and β-pinene.[97] Further, for the last two, the polymerisation rate at room temperature is strongly retarded by water concentrations between 10^{-2} and 10^{-3}M, and it has been claimed[96,97] that this result represents unambiguous evidence for intermediate ionic species in a radiation-induced polymerisation. The initiation of the polymerisation chain is thought to follow carbonium-ion formation which may occur by an ion–molecule[98] or an ion-rearrangement[97] process involving the parent molecule-ion. The occurrence of chain transfer can be explained in terms of proton transfer from the propagating ion to the monomer.[96,97] Although these radiation-induced ionic polymerisations have many overall features in common with initiation by strong Brönsted acids, it is important to recognise some essential differences. With strong acids, a concentration of carbonium ions together with their gegenions is in thermodynamic equilibrium with the acid catalyst and the olefinic base. On the other hand, direct irradiation can only lead to labile ions which must react before they are neutralised. Hence the neutralisation step must be slow to account for chain lengths, including transfer, extending up to the polymerisation of several thousand molecules per initiator. We have already seen that neutralisation can be slow in the gas phase compared with proton transfer and other ionic reactions, and here we have a similar phenomenon in solution. There have been various suggestions[95,99,100] that the electron must be "captured" by solid particles in solution in order for polymerisation to proceed; some support for this idea comes from the increase in polymerisation yields[99,100] when large quantities of solids, notably silica gel or zinc oxide, are present with the monomer (isobutene) during irradiation. However, it is far from clear what the action of these solids really represents; possibilities must include heterogeneous initiation by induced catalytic activity in the solids,[101] as well as the likelihood that polar impurities are removed from the monomer. What is more pertinent is that very high yields, G(—Monomer) *ca.* 10,000, can be obtained without recourse to the addition of foreign matter[96]. Although further work is required to resolve this question, there seems to be no compelling reason to invoke any special mechanism beyond the factors mentioned earlier in this Review to "explain" the occurrence of ionic reactions in solution.

(*iii*) *Aromatic hydrocarbons.* Compared with other hydrocarbons, these compounds show higher stability to ionising radiation, as judged by the criterion of G-yield for the disappearance of initial material. Benzene loss corresponds to a G of 0·8 for fast-electron irradiation; only very low gas yields are obtained,[102] consisting mainly of hydrogen ($G = 0{\cdot}036$) and

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[96] Best, Bates, and Ff. Williams, *Trans. Faraday Soc.*, 1962, **58**, 192.
[97] Bates, Best, and Ff. Williams, *J.*, 1962, 1531.
[98] Lampe, *J. Phys. Chem.*, 1959, **63**, 1986.
[99] Worrall and Pinner, *J. Polymer Sci.*, 1959, **34**, 229.
[100] Dalton, Glawitsch, and Roberts, *Polymer*, 1961, **2**, 419.
[101] Kohn, *J. Phys. Chem.*, 1962, **66**, 1185.
[102] Gordon and Burton, *Discuss. Faraday Soc.*, 1952, **12**, 88.

acetylene ($G = 0{\cdot}020$). Even lower yields pertain for the electron-irradiation of biphenyl[103] and the higher polyphenyls,[22] the G-yields for disappearance ranging from 0·2 to 0·3 at elevated temperatures (250—300°). Because of their combined radiolytic and thermal stability, biphenyl and terphenyl mixtures have been adopted as coolant-moderators for nuclear reactors. As mentioned earlier, the G-yields of gas and "polymer" from aromatic compounds tend to increase at higher LET (linear energy transfer), but the relative increase in polymer yield is usually much less than is found for the gas yield.[22,104] By irradiating benzene to low conversion, Gordon, Van Dyken, and Doumani[105] have been able to isolate and identify several compounds which probably act as intermediates in the formation of the polymeric condensate; these include such reactive olefins as phenylcyclohexadiene and bicyclohexadienyl, and again it is apparent that unsaturated products play an important part in secondary reactions. Only limited progress has been made in unravelling the complex distribution of products formed (in low yield—cf. above) by the radiolysis of biphenyl and terphenyls.[22] A serious discussion of reaction mechanism in these systems must await more detailed knowledge of the chemistry at low conversions.

Alkyl-substitution in the benzene ring leads to gas yields 3—5 times greater than for benzene itself,[106] but these values, G *ca.* 0·2, are still ten times lower than for the corresponding alkanes. The polymer yield from alkylbenzenes is about the same as from benzene.[76] Qualitatively, these results have been interpreted[106,107] in terms of intramolecular energy transfer from the alkyl groups to the benzene ring ("sponge" protection). This concept is equivalent to the view that the higher excited states of the molecule-ion (or neutral molecule), corresponding to σ-electron promotion, undergo rapid internal conversion, so that the chemistry becomes highly characteristic of states involving electron displacement or rearrangement of the π-electrons associated with the benzene ring.

(c) **Reactions in Polymeric Solids.**—This subject has been reviewed in detail.[108,109] In some respects, the behaviour of polymers exemplifies the general reactions we have discussed earlier. Thus the production of cross-linking and *trans*-vinylene unsaturation in amorphous polyethylene parallel the major changes sustained by liquid n-alkanes, whilst the C–C chain scission of polymers containing the repeating unit [$\cdot CH_2\cdot CRMe\cdot$] is analogous to the predominant mode of rupture shown by branched

[103] Burr and Scarborough, *J. Phys., Chem.*, 1960, **64**, 1367.

[104] Burns, *Trans. Faraday Soc.*, 1962, **58**, 961.

[105] Gordon, Van Dyken, and Doumani, *J. Phys. Chem.*, 1958, **62**, 20.

[106] Sworski, Hentz, and Burton, *J. Amer. Chem. Soc.*, 1951, **73**, 1998.

[107] Collinson and Swallow, *Chem. Rev.*, 1956, **56**, 471.

[108] Dole, Chapter 16 of "Crystalline Olefin Polymers," ed. Raff and Doak, Interscience, New York, in the press.

[109] Charlesby, "Atomic Radiation and Polymers," Pergamon, London, 1960; Chapiro, "Radiation Chemistry of Polymeric Systems," Interscience, New York, 1962.

alkanes.[36] However, it is also important to recognise some deviations from the pattern exhibited by lower hydrocarbons. For example,the 10^{-1}—10^{-2}M-concentration of initial unsaturation in polyethylene does not affect the *G*-yield of hydrogen gas, and there is no evidence to suggest that the decay of unsaturated groups is due to attack by free radicals or hydrogen atoms.[110] The disappearance of unsaturated groups in polyethylene is presumed to give rise to end- or cross-links, depending on position in the chain. Surprisingly, unsaturated polymers (polybutadiene, polyisoprene) form cross-links with only about the same efficiency as polyethylene (*G ca.* 1·0 ± 0·5) although infrared measurements testify to large decreases in unsaturation content; internal addition by "ring links" must therefore be inferred. The isomerisation of *cis*- to *trans*-polybutadiene has been observed in the solid state and in mixtures with polyethylene,[111] but the yield ($G = 14$) is much less than the free-radical-sensitised conversion in solution which proceeds to the thermodynamic equilibrium ratio. The changes in unsaturation content are difficult to interpret except on the basis of excitation-energy transfer along and across the hydrocarbon chains.

Many polymers exist partially in crystalline form, and electron-spin resonance measurements have demonstrated[112] that stable free radicals are produced by irradiation at −196°. In polyethylene, the most abundant radical is formed by loss of a hydrogen atom; the decay kinetics at room temperature correspond to a first-order relation which suggests that the radicals are formed close together in pairs and subsequently react without homogeneous interaction. Although labile at room temperature, the free radicals persist long enough to react with deuterium gas, and the rate of hydrogen-isotope exchange parallels the decay of free radicals in the system.[113] Exposure of irradiated crystalline polyethylene to oxygen leads to considerable oxidation, but this is obviated if the sample is annealed at the melting point (142°) to secure free-radical combination before the admission of oxygen. Free radicals have also been detected after irradiation of lower hydrocarbons in the solid state.[114]

Large changes in the physical properties of polymers of high molecular weight result from the introduction of a relatively small number of cross-links or cleavages in the chains.[109] There has been much speculation about the mechanism of cross-linking. In the crystalline regions there can be little doubt that free radicals are intermediates. The problem in the liquid phase is similar to that encountered in cyclohexane. The possible roles of "hot" hydrogen atoms[115] or bimolecular ionic processes[36,116] have been

[110] Dole, Milner, and Ff. Williams, *J. Amer. Chem. Soc.*, 1958, **80**, 1580.

[111] Golub, *J. Amer. Chem. Soc.*, 1960, **82**, 5093; Dole and Ff. Williams, *Discuss. Faraday Soc.*, 1959, **27**, 74.

[112] Lawton, Balwit, and Powell, *J. Chem. Phys.*, 1960, **33**, 395.

[113] Dole and Cracco, *J. Phys. Chem.*, 1962, **66**, 193.

[114] Smaller and Matheson, *J. Chem. Phys.*, 1958, **28**, 1169.

[115] A. A. Miller, Lawton and Balwit, *J. Phys. Chem.*, 1956, **60**, 599.

[116] Libby, *J. Chem. Phys.*, 1961, **35**, 1714.

widely discussed, but little differentiation is possible on the grounds of experimental evidence beyond the fact that homogeneous free-radical interaction is not applicable.[108,117]

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[117] Chapiro, *Chimie et Industrie*, 1961, **85**, 393.